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The contribution of fossil sources to the organic aerosol in the Netherlands

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HIGHLIGHTS

- First measurements of ^{14}C in organic carbon (OC) in the Netherlands.
- Modern sources dominate OC both at the urban and coastal site.
- Significantly higher $F^{14}C$(OC) at the coastal site than at the urban site.
- Clear signature of pollution long-range transport in $F^{14}C$(OC) at the coastal site.

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ABSTRACT

We measured the radiocarbon (^{14}C) content of organic carbon (OC) samples from two locations in the Netherlands, the urban location of Amsterdam and the coastal location of Petten. PM10 samples were collected in Amsterdam and total suspended particles were collected in Petten using high volume samplers. The $^{14}C/^{12}C$ fraction in the samples is reported as fraction modern ($F^{14}C$). It can be used to roughly estimate the contribution of fossil sources to OC, since $F^{14}C$ of fossil fuels is 0, whereas biogenic and wood burning sources are characterized by $F^{14}C$ values close to 1. At the coastal location organic carbon has higher $F^{14}C$ values (0.83 ± 0.04 standard uncertainty) than at the urban location (0.68 ± 0.05). A fraction modern of 0.68 is in the range of $F^{14}C$ values published for OC of other European urban areas (0.68–0.81). The coastal $F^{14}C$ of 0.83 agrees well with measurements at the coastal location of Mace Head, even though in Mace Head measurements were made on particles smaller than 1.5 μm (PM1.5). A $F^{14}C$ of 0.83 is on the lower end of $F^{14}C$(OC) values estimated for continental background sites in Europe. Fossil sources might be contributing slightly more to organic carbon in the Netherlands than in other European regions. However, a bigger data set is needed to substantiate this finding. On average, fossil fuel combustion is responsible for approximately 40% of the organic carbon in Amsterdam and approximately 20% at the coastal location. At the coastal location, $F^{14}C$ was clearly lower than average when polluted air masses reached the measurement site, whereas in the urban area, air mass history did not have a strong influence on $F^{14}C$.

1. Introduction

Organic matter constitutes a significant aerosol fraction over Europe (Putaud et al., 2010) and contains many toxins, allergens, and other harmful substances. The source apportionment of organic aerosol has therefore become an important goal in aerosol science (Mauderly and Chow, 2008). One method for source apportionment that has become increasingly popular is the measurement of the radioactive carbon isotope ^{14}C of the carbonaceous aerosol (e.g. Currie, 2000; Szidat et al., 2006).

^{14}C is produced at a relatively stable rate in the upper atmosphere through reactions initiated by cosmic rays. In the atmosphere, this cosmogenic ^{14}C ultimately forms $^{14}CO_2$, which enters the biosphere, and via photosynthesis and respiration fluxes an approximate ^{14}C equilibrium with the atmosphere is achieved. The living biosphere has therefore a characteristic ratio of $^{14}C/^{12}C$,

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which is closely linked to atmospheric $^{14}CO_2$ levels. After the death of an organism the uptake of $^{14}CO_2$ stops and ^{14}C starts to decay with a half-life 5730 years (Godwin, 1962).

The ^{14}C content of a sample is expressed as a $^{14}C/^{12}C$ ratio and reported relative to a standard of oxalic acid, whose activity is related to the activity of atmospheric CO_2 and thus of the biosphere under natural circumstances in the year 1950. Following the nomenclature of Reimer et al. (2004), we report our ^{14}C data as fraction modern ($F^{14}C$)

$$F^{14}C = \frac{\frac{^{14}C}{^{12}C}(\text{sample})}{\frac{^{14}C}{^{12}C}(1950)}.$$

The $^{14}C/^{12}C$ ratio of the sample and the standard are both background corrected and normalized for fractionation to $\delta^{13}C = -25‰$, and the standard is not corrected for decay since the year 1950.

Under natural equilibrium conditions a sample from the natural contemporary biosphere would have $F^{14}C = 1$. The situation is complicated due to two anthropogenic effects that influence the $^{14}C/^{12}C$ ratio of atmospheric CO_2, and thus of the biosphere. After 1950, nuclear bomb testing significantly increased the ^{14}C levels in the atmosphere, such that $F^{14}C$ of atmospheric CO_2 almost doubled in the Northern Hemisphere. $F^{14}C$ decreased again after the ban of above-ground bomb tests, since ^{14}C is taken up by the oceans and the terrestrial biosphere. The second anthropogenic effect on the ^{14}C activity of atmospheric CO_2 is the increasing emission of fossil-fuel derived CO_2, which does not contain any ^{14}C. The present-day value of atmospheric CO_2 is around 1.04 (Levin et al., 2010).

Measuring the ^{14}C content of an aerosol sample gives a relatively clear-cut way of finding the carbon fraction that arises from fossil sources, since in fossil fuels ^{14}C has decayed and $F^{14}C = 0$. The $F^{14}C$ of the other two major aerosol sources, namely biomass burning and secondary organic aerosol (SOA) formation from biogenic precursor gases is close to $F^{14}C$ of contemporary biomass. More precisely, SOA from biogenic precursor gases, as well as minor sources such as primary biogenic particles, cigarette smoke and cooking emissions, are expected to have $F^{14}C$ around 1.04, since they arise from living or recent biomass. The $F^{14}C$ of organic carbon from wood combustion is higher, because a significant fraction of the wood was fixed during the bomb peak in $^{14}CO_2$. Estimates of $F^{14}C$ are commonly based on tree growth models (Lewis et al., 2004; Mohn et al., 2008) and range from 1.08 to 1.30 (Szidat et al., 2006, 2009; Minguillon et al., 2011; El Haddad et al., 2011; Genberg et al., 2011; Gilardoni et al., 2011) depending on assumptions of the age of the wood, and to a lesser extent on its origin.

Most ^{14}C measurements have been conducted on the total carbonaceous fraction of PM10 or PM2.5 (e.g., Currie, 2000 and references therein; Fushimi et al., 2011; Gelencser et al., 2007; Schichtel et al., 2008; Glasius et al., 2011). However, the elemental and organic carbon fractions have different formation mechanisms and differ strongly in their radiocarbon content. Elemental carbon (EC) is formed by combustion processes and is usually dominated by fossil sources, unless there are strong biomass burning sources nearby (Szidat et al., 2007). Organic carbon (OC) on the other hand has a high contribution of secondary material, which is dominated by natural sources (e.g. Kanakidou et al., 2005; Goldstein et al., 2009), and therefore contains a higher fraction of modern carbon. Analyzing radiocarbon from OC and EC separately gives more conclusive information on the sources of carbonaceous aerosol (e.g., Szidat et al., 2006; Szidat et al. 2004a,b; Heal et al., 2011; Szidat et al., 2009; Bernardoni et al., 2012; Zhang et al., 2012).

The objective of this study is to derive the fossil fraction of OC at a coastal and at an urban background site in the Netherlands. The Netherlands is a densely populated country with high PM levels compared to other western European countries. The carbonaceous aerosol comprises 15–22% of PM10 and 18–30% of PM2.5 across various rural and urban stations. 60–90% of the total carbon resides in the fine PM2.5 fraction of the aerosol (Weijers et al., 2011). A source apportionment study (Mooibroek et al., 2011) using positive matrix factorization (PMF) receptor modeling shows that about half of the OC in the Netherlands is associated with secondary inorganic species, pointing to a secondary origin for the OC. Another major contribution comes from a mixed industrial activities/incineration source that is apparent also in rural locations, far from industrial centers and the authors therefore speculate that also domestic wood combustion contributes to this factor.

2. Experimental methods

2.1. Sampling and sampling sites

The measurements reported in this work result from a pilot study for applying radiocarbon measurements to aerosols in the Netherlands, funded by the Dutch Ministry of Infrastructure and Environment (I&M). Filter samples originate from two locations: the urban location of Amsterdam and the coastal location of Petten. The urban filter samples were provided by the Municipal Health Service of Amsterdam (GGD) and collected from January to June 2006 at the Amsterdam Overtoom station. The site is approximately 60 m from a busy road but separated by a 5-story building from the road and can therefore be considered an urban background site. The coastal filter samples were collected at the ECN site in Petten near the Coast of the North Sea, 50 km North-West of Amsterdam from July to September 2009.

At both sites filter samples were collected with high volume samplers (Graseby Andersen) on Whatman QMA quartz fiber filters (No, 1851865). At the coastal site total suspended particles (TSP) were sampled, whereas PM10 was collected at the urban site. The flow rate was 600 m^3 day^{-1} for the coastal samples (Petten) and 1630 m^3 day^{-1} for the urban samples (Amsterdam). The coastal filter samples were stored at 10 °C, wrapped in aluminum foil. The urban filter samples were stored at 20 °C according to European legislature for weighing chambers (EN 12341). Due to the routine sampling protocols following European standard procedures the filters were not pre-heated in the respective laboratories immediately prior to sampling to remove adsorbed organic material. Ten Brink et al. (2009) tested the possibility of using routine PM samples for carbon analysis and found that the adsorbed organic material on QMA quartz fiber filters taken out of the box is roughly 1–2 μg carbon per cm^2 of filter material. For short sampling times this constitutes a non-negligible fraction of the organic carbon sample and has to be corrected for.

2.2. Extraction of OC for radiocarbon analysis

For radiocarbon analysis the organic carbon in the filter sample is converted to CO_2 by combustion in O_2 and separated from other interfering gases. Fig. 1 shows the experimental setup which is similar to the THEODORE (two-step heating system for the EC/OC determination of radiocarbon in the environment) setup described by Szidat et al. (2004c). Briefly, the system consists of two subsystems, a combustion tube, where the CO_2 is formed, and the CO_2 collection line. The combustion tube is made of quartz glass and surrounded by three ovens, the first at a temperature of 340 °C, the other two at 650 °C and the last oven is filled with a platinum

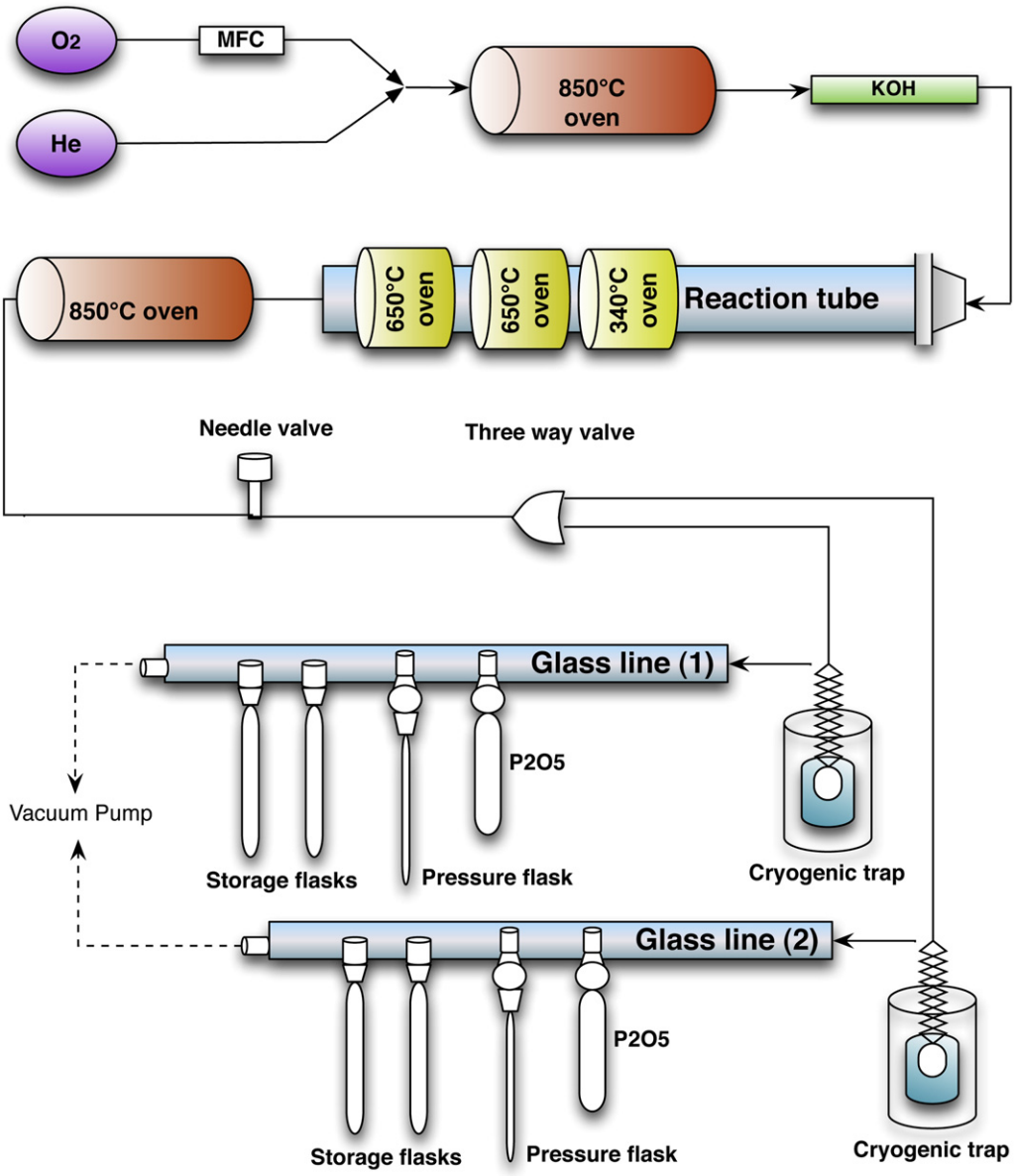

Fig. 1. Schematic of the CO_2 extraction line.

catalyst for complete oxidation of organic compounds to CO_2. After the combustion tube there is an additional oven filled with CuO wires at 850 °C. The CO_2 collection system is connected to the combustion tube via a needle valve and a CO_2 trap cooled in liquid nitrogen. The needle valve regulates the pressure in the combustion tube to 1100 ± 50 mbar and the O_2 carrier gas flow in the system to 60 ml min^{-1}. The carrier gases are pre-cleaned using an oven filled with NiO wires at 850 °C followed by a tube containing KOH. Oxygen then flows through the combustion tube and via the needle valve to the CO_2 collection line where it is pumped through the CO_2 collection trap by a vacuum pump. The pressure in the CO_2 collection line is below 30 mbar to prevent condensation of O_2 in the liquid nitrogen trap.

For the extraction of OC from the filter sample, a filter piece of around 25 cm^2 is placed in the movable filter holder in the combustion tube. The filter is then introduced into the 340 °C oven for 15 min in continuous O_2 flow. This is a common extraction temperature for OC, whereas typical extraction times in the literature range from 10 to 20 min (Minguillon et al., 2011; Genberg et al., 2011; Szidat et al., 2004c; Heal et al., 2011; Zhang et al., 2010). Szidat et al. (2004c) and Zhang et al. (2012) show that $F^{14}C$(OC) stays stable over a range of extraction temperatures. The extraction times used in the literature are usually sufficient to capture most organic carbon (see Zhang et al., 2012). Therefore our choice of extraction should ensure comparability with previously published data.

The combustion products pass the oven with platinum catalyst and the oven filled with CuO to completely oxidize all organic compounds to CO_2. Subsequently, the CO_2 and other reaction products with sufficiently low vapor pressures are frozen out in the liquid nitrogen trap, while O_2 is pumped away. After 15 min, the collected gases are released from the trap. Water vapor is removed by chemical reaction with P_2O_5 and nitrous oxides (resulting from the combustion of ammonium nitrate and ammonium sulfate) are removed by equilibrating the sample with CeO_2 for 30 min at 650 °C. Then the CO_2 (including still possible traces of SO_2) is sealed in glass ampoules and sent off for Accelerator Mass Spectrometry (AMS) analysis.

2.3. AMS measurements of ^{14}C

Graphitization and AMS measurements are performed at the AMS facility of the Centre for Isotope Research (CIO) at the University of Groningen. The CO_2 sample is (first) heated in the presence of Sulfix®, a mixture of cobalt oxide and silver oxide, at 500 °C for three hours to remove possible sulfur compounds. The graphitization system consists of a cold finger, a small reaction tube, and a pressure sensor. A porous iron pellet (de Rooij et al., 2010) is placed in the reaction tube and the CO_2 sample and H_2 are added to the system at the molecular ratio H_2/CO_2 of 2.5. Then, CO_2 is reduced to graphite on the iron pellet at 600 °C. Meanwhile, Peltier cooling elements cryogenically remove the water vapor formed during the graphitization reaction. The graphitization yield is virtually 100%, only for the smallest samples (<30 μg) the yield is somewhat lower (≈90%). After graphitization, the pellet is pressed into 1.5 mm target holders.

The AMS system is a high-throughput mass spectrometer, dedicated to ^{14}C measurements (van der Plicht et al., 2000). It simultaneously measures $^{14}C/^{12}C$ and $^{13}C/^{12}C$ ratios. Samples are analyzed in batches that contain also oxalic acid (HOxII) calibration material and of ^{14}C-free reference materials (graphite and ^{14}C-free CO_2 gas) that cover the same mass range as the samples. The $^{14}C/^{12}C$ ratios of each sample is reported in Percent Modern Carbon and normalized for fractionation to $\delta^{13}C = -25‰$ using its AMS-measured $\delta^{13}C$-value. An increase in $F^{14}C$ of the ^{14}C-free reference materials, and a decrease in $F^{14}C$ of the HOxII is observed with decreasing sample size. This mass dependence is largely due to contamination during the extraction, graphitization, and AMS measurement. The deviation from the nominal $F^{14}C$ values of the standards can be used to quantify the contamination with modern and fossil carbon, respectively, and corresponding corrections are applied to the samples (de Rooij et al., 2010). With the set-up used in this study, the modern carbon contamination during the graphitization process is between 0.15 and 0.35 μg C. The fossil carbon contamination is around 1.5 μg C. The fossil and modern carbon contamination of extraction and graphitization combined are typically 2–4 μg, compared with typical sample sizes of 80–400 μg. Since the standard and background samples were extracted exactly as the aerosol filter samples, the correction method outlined above also corrects for typical contamination during extraction and combustion.

2.4. Filter blanks

The amount of carbon on an unheated filter directly out of the box was approx. 1 μg carbon cm^{-2} of filter material. Two field blanks, which also contain contamination introduced during sampling, weighing and storage, had somewhat higher carbon amounts, namely 1.5 and 2.0 μg carbon cm^{-2}. Since the amount of carbon on blank filters can vary significantly (Ten Brink et al., 2009) we assume 1.5 μg carbon cm^{-2} with an uncertainty of ±50% for the blank correction. A $F^{14}C(OC)$ of 0.39 was measured on the pooled CO_2 extracted from two different unheated filters. One of the field blanks was also analyzed for ^{14}C and yielded a somewhat higher $F^{14}C(OC)$ of 0.48. Since we analyzed only one blank sample each, the variability of $F^{14}C(OC)$ for the unheated filter and the field blank is unknown. One of the few publications that report the $F^{14}C$ values of field blanks (Fushimi et al., 2011) shows that the variation in $F^{14}C$ of the blank filters is much smaller than the variation in carbon amount on the filters. Therefore, we choose $F^{14}C(OC)$ of the field blank for correction with an uncertainty of ±30%, resulting in $F^{14}C(OC) = 0.48 \pm 0.14$%.

3. Results and discussion

Table 1 shows $F^{14}C(OC)$ before and after blank correction for individual samples collected in the urban area of Amsterdam and the coastal location of Petten. The amount of carbon on a blank filter (1.50 ± 0.75 μg C cm^{-2} of filter material) was significant compared to the typical filter loading, which varied between 3 and 16 μg C cm^{-2}. The $F^{14}C(OC)$ of the blank is significantly lower than $F^{14}C(OC)$ of typical aerosol samples and therefore the corrected $F^{14}C$ values are mostly higher than the uncorrected ones. The final uncertainty of the corrected $F^{14}C$ values varies between 2 and 22% of the sample $F^{14}C$ and is dominated by the uncertainties introduced through the blank correction.

Table 1 also shows concentration of PM_{10} and the concentration of OC that was extracted for ^{14}C analysis. However, it must be kept in mind that not all the OC is desorbed at 340 °C and the concentrations of organic carbon measured with standard methods could be up to 30% higher (e.g. 75–85% recovery of OC at 375 C; Zhang et al., 2012).

The fraction modern of OC is higher at the coastal site of Petten than it is in the city of Amsterdam (Fig. 2, gray bars). The average and standard deviation of $F^{14}C$ over all samples are 0.68 ± 0.17 in Amsterdam and 0.86 ± 0.13 in Petten. The difference is significant at the 95% confidence level (Anova, singe factor). This shows that the fossil contribution to the carbonaceous aerosol is higher at the urban site. The quantitative difference, however, should not be over-interpreted, because the ^{14}C measurements were carried out on different aerosol fractions (TSP versus PM10) and during different periods. It is plausible that TSP samples contain more modern carbon than PM10 samples due to the presence of coarse biogenic particles such as pollen, that are found to a lesser extent in PM10. Also, $F^{14}C(OC)$ could vary temporally, although contrary to $F^{14}C(TC)$ it usually does not show a very strong seasonal trend in the places where this has been studied (Table 2).

The fossil fraction of OC can be derived by dividing $F^{14}C(OC)$ by the fraction modern of contemporary OC ($F^{14}C_{cont}$), if several assumptions are made. We approximate the $F^{14}C_{cont}$ as a weighted average of $F^{14}C$ of biomass burning carbon ($F^{14}C_{bb}$) and $F^{14}C$ of biogenic carbon ($F^{14}C_{bio}$). Therefore, we need to estimate $F^{14}C_{bb}$, $F^{14}C_{bio}$, and the relative contribution of biomass burning to OC (f_{bb}). Since values of $F^{14}C_{bb}$ vary widely in the literature, we assume a lower and a higher limit: 1.1 and 1.25, respectively. We represent $F^{14}C_{bio}$ by $F^{14}C$ of atmospheric CO_2 measured at the Schauinsland station (Levin et al., 2010) in the year and season the samples were taken. In 2006 spring and 2009 summer these values are both roughly 1.05. f_{bb} in the Dutch spring and summer is unknown, but values published in the literature for central and northern Europe tend to vary between 0.1 and 0.2 (Szidat et al., 2006, 2009; Minguillon et al., 2011; Heal et al., 2011). However, f_{bb} can be significantly higher in wintertime (Szidat et al., 2007; Bernardoni et al., 2012). For spring and summer in the Netherlands we choose a lower limit of no biomass combustion ($f_{bb} = 0$) and an upper limit of $f_{bb} = 0.3$. This results in an average fossil fraction of OC in Amsterdam between 0.36 (no biomass burning) and 0.39 (high biomass burning: $f_{bb} = 0.3$, $F^{14}C_{bb} = 1.25$) and in Petten between 0.18 and 0.23. The fossil fractions assuming an intermediate case ($f_{bb} = 0.15$, $F^{14}C_{bb} = 1.15$) are given in Table 1.

Compared to other locations in Europe (Table 2), $F^{14}C(OC)$ in Amsterdam is at the lower end of the urban stations in central and Northern Europe, indicating a relatively high fossil fraction of OC. It is similar to Göteborg, but lower than in Zürich or Birmingham. Recent studies from urban areas in Southern Europe report higher fossil fractions in OC more in the range of our Amsterdam values (0.32–0.44 for Milan (Bernardoni et al., 2011, 2012), 0.37 for Marseille (El Haddad et al., 2011), 0.40–0.48 for Barcelona (Minguillon et al., 2011). However, it is difficult to accurately compare fossil fractions among different publications, because each study uses different assumptions of $F^{14}C_{cont}$ and it would be advisable to also report directly measured $F^{14}C$ values. The $F^{14}C(OC)$ data at the

Table 1
Results for PM10 (urban background location) and TSP (coastal location), together with OC, $F^{14}C$(OC), and rough meteorological indicators, for all filters measured. OC refers here to the fraction of the organic carbon extracted from the filters as CO_2 during combustion in O_2 at 340 °C. $F^{14}C$ raw and $F^{14}C$ corr refer to $F^{14}C$(OC) of the sample before and after blank correction, respectively (blank: 1.50 ± 0.75 μg C cm^{-2} of filter material, $F^{14}C = 0.48 \pm 0.16\%$). The fossil fraction is calculated assuming a contemporary $F^{14}C$ of 1.065 (see text).

Amsterdam, urban								
Sampling dates 2006	PM_{10} (μg m^{-3})	OC (μg m^{-3})	$F^{14}C$ raw	$F^{14}C$ corr	$F^{14}C$ 1σ	Fossil fract	Rain (mm)	Air mass
19/01 00:00 – 20/01 00:00	33.3	1.8	0.73	0.79	0.04	0.26	0.0	Mixed
11/03 00:00 – 12/03 00:00	26.7	2.1	0.70	0.76	0.05	0.28	3.1	Mixed
19/03 00:00 – 20/03 00:00	37.5	1.4	0.57	0.60	0.05	0.43	0.0	Clean
27/03 00:00 – 28/03 00:00	22.0	2.0	0.58	0.60	0.03	0.44	3.1	Poll.
05/04 00:00 – 06/04 00:00	17.6	1.5	0.49	0.49	0.04	0.54	4.6	Clean
19/05 00:00 – 20/05 00:00	25.7	2.3	0.68	0.72	0.03	0.33	4.0	Poll.
27/05 00:00 – 28/05 00:00	21.3	1.4	0.62	0.66	0.05	0.38	7.4	Poll.
04/06 00:00 – 5/06 00:00	29.8	1.5	0.91	1.05	0.10	0.02	0.0	Mixed
8/06 00:00 – 9/06 00:00	36.4	2.1	0.46	0.45	0.02	0.57	0.0	Clean
12/06 00:00 – 13/06 00:00	24.6	3.5	0.62	0.64	0.02	0.40	0.0	Poll.
		Averages			St. dev.			
All	27.5	2.0	0.64	0.68	0.17			
Clean	30.2	1.7	0.64	0.69	0.22			
Poll	23.3	2.3	0.62	0.66	0.05			
Rain	22.7	1.9	0.61	0.65	0.11			
No rain	32.3	2.1	0.66	0.71	0.23			
Petten, coastal								
Date start 2009	TSP (μg m^{-3})	OC (μg m^{-3})	$F^{14}C$ raw	$F^{14}C$ corr	$F^{14}C$ 1σ	Fossil fract	Rain (mm)	Air mass
27/07 13:45 – 28/07 18:15	36.2	1.8	0.82	1.00	0.16	0.06	3.1	Mixed
28/07 18:20 – 29/07 18:20	59.0	3.2	0.63	0.68	0.05	0.36	0.0	Poll.
29/07 18:25 – 31/07 20:30	33.6	1.8	0.75	0.82	0.05	0.23	6.0	Mixed
01/08 10:00 – 02/08 10:00	42.3	5.5	0.72	0.75	0.03	0.29	3.8	Poll.
10/08 10:52 – 11/08 10:45	36.0	2.6	0.91	1.09	0.14	−0.03	4.6	Mixed
24/08 09:51 – 25/08 09:50	56.8	7.9	0.76	0.79	0.02	0.26	0.5	Poll.
14/09 18:00 – 16/09 10:00	50.4	4.8	0.82	0.86	0.02	0.20	0.4	Mixed
16/09 11:00 – 17/09 10:55	18.6	1.6	0.68	0.86	0.19	0.20	0.0	Clean
		Averages			St. dev.			
All	41.6	3.6	0.76	0.86	0.13			
Clean	32.2	2.4	0.78	0.91	0.11			
Poll	52.7	5.5	0.70	0.74	0.05			
Rain	37.0	2.9	0.80	0.92	0.16			
No rain	46.2	4.4	0.72	0.80	0.08			

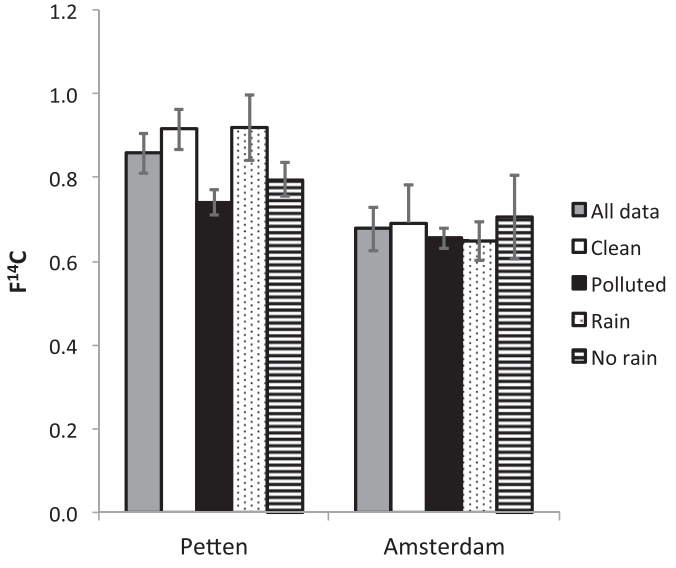

Fig. 2. Averages of $F^{14}C$(OC) in Amsterdam and Petten, for all data, clean and polluted time periods and rainy and dry periods. The error bars refer to the standard error of the mean. If the standard errors do not overlap, the difference between the means is usually considered significant. However with small samples sizes as used here, the standard errors should be considered with caution and be more regarded as a rough indication.

coastal station in Petten are higher than $F^{14}C$(OC) at another coastal station in Mace Head under conditions of continental pollution. They are lower than $F^{14}C$(OC) estimated for clean marine samples collected on a ship in the NE Atlantic and in Mace Head for clean marine air mass conditions. During the sampling time in Petten, we encountered both fairly clean but also polluted conditions, which is

Table 2
Comparison of $F^{14}C$(OC) values measured in various locations in Europe.

Location	$F^{14}C$	Type	Season	PM fraction	Ref.
Amsterdam	0.68	Urban	Jan–June	PM10	This work
Birmingham	0.76	Urban	All seasons	PM2.5	Heal et al., 2011
Göteborg	0.68	Urban	Winter	PM10	Szidat et al., 2009
Göteborg	0.70	Urban	Summer	PM2.5	Szidat et al., 2009
Zürich	0.76	Urban	Summer	PM10	Szidat et al., 2006
Zürich	0.79	Urban	Winter	PM10	Szidat et al., 2006
Zürich	0.81	Urban	Spring	PM10	Szidat et al., 2006
Barcelona	0.64	Urban	Winter	PM1	Minguillon et al., 2011
Barcelona	0.55	Urban	Summer	PM1	Minguillon et al., 2011
Raö	0.71	Rural	Winter	PM2.5	Szidat et al., 2009
Montseny	0.73	Rural	Winter	PM1	Minguillon et al., 2011
Montseny	0.80	Rural	Summer	PM1	Minguillon et al., 2011
NE Atlantic clean	0.89	Marine	Apr–July	PM1.5	Ceburnis et al., 2011
Mace head poll.	0.77	Coastal	Mai, Sept, Oct	PM1.5	Ceburnis et al., 2011
Petten	0.83	Coastal	Jul–Sept	PM10	This work

consistent with these intermediate values for $F^{14}C(OC)$ compared with the only other coastal station where ^{14}C was measured in OC.

Radiocarbon data for OC are relatively few. Gelencser et al. (2007); Yttri et al., 2011; Genberg et al., 2011) combine $F^{14}C(TC)$ with other data to derive fossil contributions to primary and secondary OC and EC separately. Their data can be converted to fossil fractions for OC, which range from 0.06 to 0.17 for the summer season, which is slightly lower than the fossil contribution measured in Petten.

For each filter sample we calculated 3-day air mass back trajectories including precipitation along the trajectory, using the NOAA Hysplit model (Draxler and Rolph, 2013). We classified the air masses arriving at the measurement site in three categories: 'Clean' trajectories originated from marine areas with little time spent over land. 'Mixed' trajectories are marine air masses that had some contact with land, such as Southern England or Denmark, or air masses that originated in remote continental locations. 'Polluted' trajectories spent some amount of time over polluted regions in the Netherlands, Belgium or Germany (Ruhr area). Polluted samples were characterized by air mass conditions that experienced polluted trajectories at least 50% of the time. The amount of rain calculated along the trajectory during the last 24 h is given in Table 1. If the amount of rain along the trajectory exceeded 1 mm, the trajectories were classified as 'rainy'. The time window of 24 h was chosen to characterize possible recent washout of pollutants. At the coastal site most filter samples were characterized by mixed trajectories. There was one 'clean' case with air mass back trajectories directly from the North, which is also clearly identified by very low TSP concentrations.

At the coastal site the average $F^{14}C(OC)$ was lower during polluted time periods than during mixed periods (Fig. 2). In fact, the lowest three values of $F^{14}C(OC)$ during the measurement period were encountered during polluted conditions (Table 1) and they approach the values measured in the urban area of Amsterdam. Despite the few data points in this comparison this gives an indication that fossil fuel emissions in the industrialized areas around the Netherlands can impact on $F^{14}C(OC)$ in TSP. Nevertheless, even in polluted conditions the majority of the organic carbon comes from modern sources with the fossil contribution on average below 20% at the coastal site. Rain along the trajectory also seems to increase $F^{14}C(OC)$, though not significantly. This is likely due to the limited aerosol samples available for this study and the fact that more of the rain events occurred during mixed conditions than during polluted conditions. In polluted conditions the air masses usually arrive from the Southeast and rainfall is less common.

At the urban site neither air mass history nor rain events seem to have a strong influence on $F^{14}C(OC)$ (Fig. 2). This suggests that local influences at the urban site outweigh the effect of long-range transport. Unexpectedly, PM10 concentrations are on average higher for samples characterized by mixed/clean trajectories than by polluted trajectories (Table 1). However there was also more rain during polluted conditions and the local influence of a busy street canyon to the North of the sampling site might complicate the situation. Samples that were collected during rainy periods showed significantly lower PM10 concentrations, because the aerosols are removed by the precipitation and because rainy periods are often associated with a transition to cleaner air masses. However, there is no significant effect of rain on $F^{14}C(OC)$.

Fig. 3 shows a scatter plot of $F^{14}C(OC)$ vs. PM10 concentrations for the urban and coastal site. At the coastal site (Fig. 3a) there is no discernable correlation between aerosol mass concentration and $F^{14}C(OC)$, since the range of TSP concentrations during polluted conditions overlaps somewhat with the range during mixed air mass conditions. In contrast to TSP, $F^{14}C(OC)$ shows a distinction between polluted and clean/mixed air mass conditions, with lower

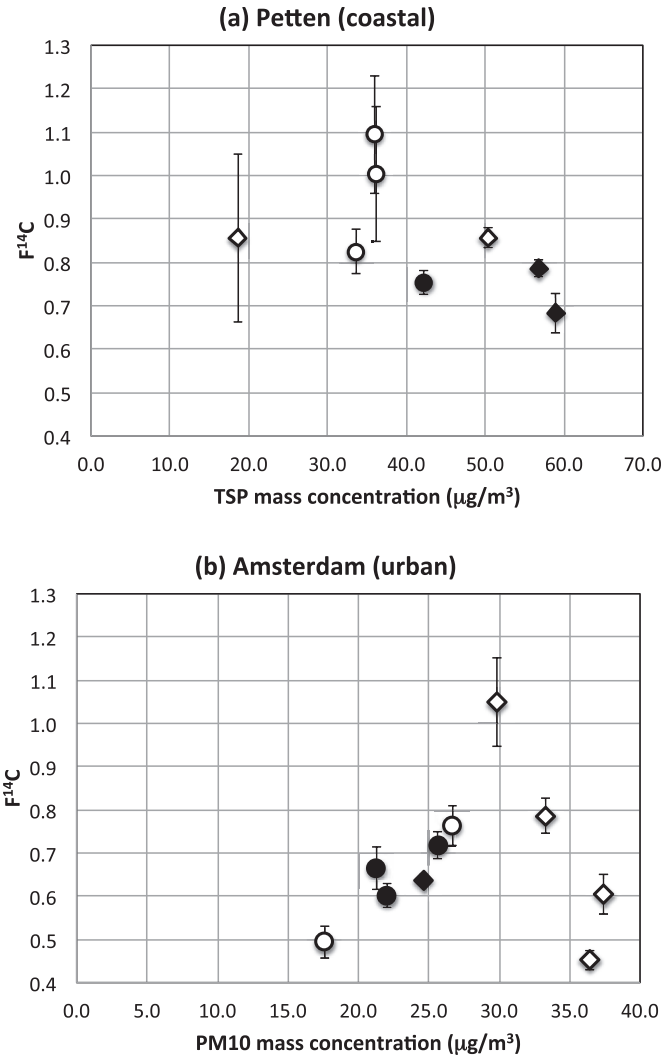

Fig. 3. $F^{14}C(OC)$ related to PM10 (Amsterdam) and TSP (Petten) mass concentration. The marker fill refers to air mass condition clean/mixed (white), polluted (black). The marker shape refers to precipitation along the trajectory: no rain (diamonds), rain (circles).

$F^{14}C(OC)$ values during polluted conditions (see also Fig. 2). This would imply that the signature of fossil anthropogenic pollution seems better preserved in the ^{14}C content than in absolute mass concentrations though this conclusion is still uncertain, because of the limited number of data points.

Despite the large uncertainty $F^{14}C(OC)$ of the only sample collected under clean conditions seems lower than some $F^{14}C(OC)$ in mixed air masses and could be comparable to polluted air masses. A similar trend can be seen when previous data sets collected in different environments are compared with each other. Samples taken in the NE Atlantic (Ceburnis et al., 2011) show that $F^{14}C(TC)$ of the clean marine background aerosol can be lower than some of the $F^{14}C(TC)$ published for continental background sites in the summer (Gelencser et al., 2007; Genberg et al., 2011; Yttri et al., 2011). Ceburnis et al. (2011) concluded that even in a remote marine location there is a measurable influence of fossil sources on the aerosol carbon. Moreover, since OC concentrations in the marine background aerosol are low, $F^{14}C(OC)$ values will be sensitive to local and regional fossil emissions, such as ship traffic around England. Such an influence could explain the reduced $F^{14}C(OC)$ value at the coastal site in the Netherlands compared to a clean marine

site. The most likely explanation for the very high $F^{14}C(OC)$ values observed in some mixed air masses is that the air mass had some contact with land and terrestrial sources added significant amounts of modern carbon to the aerosol and therefore increased $F^{14}C(OC)$.

As discussed above, the influence of air mass history on PM10 concentrations or $F^{14}C(OC)$ is obscured by local effects at the urban station (Fig. 3b). However, during rainy conditions PM10 is on average 10 $\mu g\ m^{-3}$ lower than during dry conditions. For conditions with PM10 concentrations below 30 $\mu g\ m^{-3}$, $F^{14}C(OC)$ seems to increase with PM10 concentrations. This unexpected finding is difficult to explain based on the limited amount of data, as it would suggest that in this concentration range, modern carbon would be associated with higher levels of pollution. One could speculate that conditions associated with higher PM10 values also are favorable for SOA formation from biogenic precursors. Or it is possible that the urban PM10 levels in these cases are mainly elevated by the import of rural aerosol. Precipitation might play an additional role, but more data are needed to investigate this possible effect. At the highest PM10 values, the correlation changes, and $F^{14}C(OC)$ decreases again with increasing PM10, indicating, as expected, an increasing importance of fossil sources at high pollution levels at the urban site.

4. Conclusions

We assessed the merit of measuring the radioactive carbon isotope ^{14}C in organic aerosol samples in the Netherlands in a pilot study. The aerosol samples were taken at a coastal site (TSP samples) and urban background site (PM10 samples) with high volume samplers. Despite the limited number of samples, several clear conclusions can be drawn. The average $F^{14}C(OC)$ values were higher at the coastal site (0.86) compared to the urban background site (0.68). Both at the urban site and at the coastal site the majority of OC originates from modern sources. At the coastal site, $F^{14}C(OC)$ values are on average lower in contaminated air masses than in clean air masses, as expected for an anthropogenic source. At the urban site, the air mass history has no clear effect on $F^{14}C(OC)$, but we observed an interesting correlation with PM10 levels. For PM10 values above 30 $\mu g\ m^{-3}$, $F^{14}C(OC)$ decreases with PM10, clearly illustrating the role of anthropogenic fossil carbon emissions under these conditions. However, unexpectedly the $F^{14}C(OC)$ values also decrease again toward lower PM10 values below 30 $\mu g\ m^{-3}$. It is not possible to clearly interpret this observation with the few samples available; precipitation may be an important factor.

Additional measurements could confirm our observation that $F^{14}C(OC)$ of the Dutch samples tends to fall in the lower range of measurements at various sites in central and northern Europe, showing a somewhat larger fraction of fossil carbon in this densely populated area. Even though TSP were collected for the coastal samples, $F^{14}C(OC)$ values agree well with another coastal site and for polluted conditions approach the values measured on PM10 in the urban area of Amsterdam. This suggests that the inclusion of big biogenic particles in TSP samples does not skew the $F^{14}C(OC)$ values drastically. For dedicated ^{14}C measurements, it is recommended to preheat the commercially available filters before sampling to reduce the filter blank, which constitutes the largest contribution to the measurement uncertainty in this study.

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